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Short communication

Solar-light driven photocatalytic conversion of *p*-nitrophenol to *p*-aminophenol on CdS nanosheets and nanorods



Azam Khan ^a, Zia-ur- Rehman ^{a,*}, Abdullah Khan ^b, Hina Ambareen ^a, Haseeb Ullah ^a, Syed Mustansar Abbas ^c, Yaqoob Khan ^d, Rajwali Khan ^e

^a Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

^b U.S.-Pakistan Center for Advanced Studies in Energy, NUST, Islamabad, Pakistan

^c Department of Energy and Materials Engineering, Dongguk University, 30, Pildong-ro 1gil, Jung-gu, Seoul 100-715, Republic of Korea

^d Nanosciences and Catalysis Department, National Centre for Physics, Quaid-i-Azam University campus, Islamabad 45320, Pakistan

^e Department of Physics, Abdul Wali Khan University, Mardan 23200, KPK, Pakistan

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ABSTRACT

A simple synthetic protocol devoid of toxic surfactants was applied for the synthesis of CdS nanosheets and nanorods by thermolyzing *bis*(4-benzylpiperadine-1-carbodithioate- κ^2 S, S') cadmium(II) (1) and propane-1,3-diyl *bis* (piperidincarbamodithioate)cadmium(II) (2) using ethylenediamine (en) as a solvent. The as obtained products were characterized by TEM, PXRD, and UV–Visible spectroscopy. The nanosheets (1) and nanorods (2) were confirmed by HR-TEM with a lattice spacing of 0.33 nm which corresponds to the 002 plane of hexagonal CdS, observations in consonance with XRD. Based upon the band gap obtained from UV–Vis, 2.91 eV (nanosheets) and 2.65 eV (nanorods), these nanoparticles (NPs) were used as solar light driven photocatalyst for the conversion of *p*-nitrophenol to *p*-aminophenol. The nanorods (8 min) were found slightly more efficient than nanosheets (10 min), and the conversion efficiency of both remained above 92% even after 3rd cycle without any structural damage as revealed by the afterward PXRD. The better catalytic activity of both morphologies can be attributed to quantum size effect and good optical absorbance.

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The organic contaminants present in the agricultural and industrial waste-water is adversely affecting the environment. The nitroaromatic compounds are probably the more frequent and stable enough against the natural degradation process due to their chemical and biological stability. The removal of these environmentally displeasing compounds has been done through several processes namely photocatalytic degradation, biodegradation electro-fenton, electrochemical treatment and so on [1–4]. Among the nitroaromatic compounds *p*-nitrophenol is a major organic pollutant, so the conversion of this disagreeable chemical to *p*-aminophenol is of great industrial significance as the latter is used for the production of aniline, paracetamol, phenacetin and acetanilide [5]. This reaction of environmental and pharmaceutical value was first reported by Pal in 2002 in the presence of Ag nanoparticles and BH⁻₄ [6]. After then many other noble metals such as Pt, Pd, Ru, Au and certain metal alloys have been used to catalyze this reaction [7]. Nitrogen doped graphene, metal organic frameworks (MOFs) and nanoparticles embedded metal organic frameworks have also been studied as catalyst for the

* Corresponding author. *E-mail address:* zrehman@qau.edu.pk (Z.- Rehman). conversion of *p*-nitrophenol to *p*-aminophenol [8–10]. However, the industrial applicability of these catalysts is hampered by their high cost, toxicity and recyclability. Therefore, the development of an economical and efficient reaction route is yet an unresolved dilemma. The use of metal chalcogenides as photocatalyst, which harvest the abundant and inexhaustible solar energy, is a green and promising strategy for such reactions. The direct and narrow band gap of CdS (\approx 2.4 eV) brands it a reliable chalcogenide that can be used as a visible light driven photocatalyst [11]. Additionally, the conduction band (CB) position of CdS is sufficiently negative which allow the facile electron transfer from their surface to the adsorbed molecule [12]. The phenomenon of quantum size effect (arises by reducing the particle size and specific morphology) changes the electronic states of the CdS, shifting the CB position further to a more negative value, and thus triggering the photocatalytic activity [13].

There are only few reports regarding the visible light driven photocatalytic conversion of *p*-nitrophenol to *p*-aminophenol. Agileo et al. used CdS nanorods and nanofibers for this reaction and the conversion was achieved in 270 min and 30 min, respectively [11,14]. Pahari et al. tested CdS nanoflowers for this reaction under the household CFL lamp, and achieved the conversion in 90 min [15]. Few research groups also tested CdS-based composite materials under visible light, including CdS-TiO₂, CdS/graphene hybrid and noble metal deposited CdS [16–18].

We adopted a single source precursor strategy for the synthesis of CdS NPs by simply refluxing two new cadmium(II) dithiocarbamates using ethylenediamine (en) as a solvent and thermolyzing agent devoid of any toxic capping agent/surfactant. The synthesis of the ligand salts, precursor complexes and their conversion to CdS NPs was carried out by our previously reported methods [19,20] and is schematically shown in Scheme 1. The detailed experimental procedure about the precursor synthesis, their conversion to CdS NPs and photocatalytic conversion of the *p*-nitrophenol to *p*-aminophenol by CdS nanostructures are given in supporting information.

Complex **1** and **2** were easily synthesized at ambient conditions by simply mixing the metal salt and ligand. Complex **1** was found soluble in $CHCl_3$, DMSO and DMF and hence characterized by NMR, however, for **2** only FT-IR was done due to insolubility in common organic solvents.

The bonding nature and coordination mode of the dithiocarbamate can be assessed by the stretching frequencies. The presence of bands at 347 cm⁻¹ (1) and 334 cm⁻¹ (2) assignable to Cd—S stretch [21], and a single peak for CS at 991 cm⁻¹ (**1**) and 967 cm⁻¹ (**2**) indicated the bidentate dithiocarbamate-Cd coordination. Furthermore, the C—N stretch observed at 1478 cm⁻¹ (**1**) and 1513 cm⁻¹ (**2**), values in between single and double bonds signifying the resonance phenomena in the CNSS moiety [22]. The assignment of the proton resonances was made by their peak multiplicity, intensity pattern and comparison of the integration values with the expected composition. In the complex CdL1, multiplets for phenyl protons (7.12-7.32 ppm) and methine proton (1.4–1.51 ppm), a triplet and quartet for piperidine ring protons (3.24 and 1.75 ppm), and a doublet for methylene protons (4.66 ppm, J = 5.0 Hz) was observed. In ¹³C NMR, an upfield shift of around 9 ppm in the SCS peak in complex than the free ligand confirmed the ligand coordination to metal center [23]. The remaining signals matched well with the expected composition.

The CdS NPs were obtained from the complexes **1** and **2**, single source precursors (SPs). The presence of metal-chalcogen bond template in SPs play a significant role in controlling the stoichiometry and shape of the nanocrystals [24,25]. Additionally, the different binding strength of the ligands may be responsible for dissimilarity in the stability of precursors or decomposition kinetics; hence this anomalous

decomposition pattern can be exploited to control size and morphology of the NPs [26]. In this study, the conversion of two precursors has resulted in two distinct morphologies i.e. nanosheets and nanorods. The low magnification TEM image of CdS-1 presents very thin sheets like morphologies (Fig. 1a and b). The sheets seem to be continuous and extend to several hundred micrometers in length and width. The transparent image suggests the transmission of electrons through sheets of thickness less than 5 nm. No evident boundary among the individual sheets suggests stacking over one another. The TEM image of CdS-2 shows nanorods of almost 80 nm in length and 4-6 nm in diameters (Fig. 1d and e). Moreover, the nanorods have homogeneous shape and are structurally uniform. In the HRTEM images (Fig. 1c, and f), a lattice spacing of 0.33 nm was measured for both morphologies which correspond to the 002 plane of hexagonal CdS confirming their preferential growth along the *c*-axis. The formation of different morphologies can be attributed to different solubility/stability of the precursors used. It was observed that the precursor CdL-1 completely dissolved at 60 °C in en and at 70 °C the solution turned slightly turbid due to nucleation of the CdS monomers resulting in individual CdS dot formation. A gradual increase in the temperature resulted in more CdS dots formation that probably adopted spherical assembly through common crystallographic facet {111} and then at the en boiling point (b.p) grew into sheet-like structure in {111} direction through oriented attachment [15]. However, due to insolubility of the complex CdL-2 in en upto 117 °C no nucleation was observed. Nonetheless, at en b.p, the precursor CdL-2 instantly decomposed by a nucleation burst in the earlier moment of reaction, provided the kinetic drive for anisotropic particles growth or CdS nanorods [27]. Energy dispersive X-ray spectroscopic (EDS) analysis has confirmed the presence of Cd and S in the ratio of 1:1 for both nanosheets and nanorods.

X-ray powder diffraction analysis has been carried out to understand the identity and phase purity of CdS-1 and CdS-2 nanostructures (Fig. 2). All the XRD reflections correspond to the hexagonal phase of CdS consistent with the standard JCPDS card No. 01-077-2306. The diffraction pattern show that both NPs are devoid of any detectable impurities or any other CdS phase. Compared to the standard, the 002 reflections in both diffraction patterns is of highest intensity indicating their preferential growth along the *c*-axis. Moreover, broader peaks are indicative of a small primary particle size.

UV–Visible absorption measurement is an important technique to assess the optical properties of the semiconductors NPs. The absorption



Scheme 1. Synthesis of complexes 1 and 2 and their conversion to CdS1 and CdS2 NPs.



Fig. 1. Typical TEM images of CdS-1 (a & b) and CdS-2 (d & e) at different magnifications. HRTEM images of CdS-1 (c) and CdS-2 (f), inset of (c) and (f) show lattice fringes of CdS-1 and CdS-2 NPs.

edges for nanosheets and nanorods were observed at 425 nm and 467 nm, respectively (Fig. 3). The relationship between the optical band gap (Eg) and wavelength (λ) (i.e. Eg = 1240/ λ) was used to calculate the optical band gap, and was found to be 2.91 eV (nanosheets) and 2.65 eV (nanorods). The blue-shift in optical band gap of both nanosheets and nanorods than bulk CdS (2.42 eV) is assignable to quantum size effect. The sharp absorption edge of nanorods predicts size uniformity, which is in agreement with TEM. Moreover, the nanorods show strong photo-absorption from visible to ultraviolet region than nanosheets, suggesting good photocatalytic potential of the former [28], a point well evident in the photocatalytic conversion of *p*-nitrophenol to *p*-aminophenol.

The unique photochemical and photophysical properties of CdS NPs have attracted intense interest in recent years for photocatalysis [29,30], a reaction in which electron-hole pairs are generated when light of energy (hv) equal to or greater than the band gap impinge on the semiconductor surface. For the conversion of *p*-nitrophenol to *p*-aminophenol, the amination of nitro group takes place by taking the conduction band electrons from CdS and H⁺ from NaBH₄. The photogenerated hole in the CdS valence band is filled by electrons generated by the decomposition of NaBH₄. The synthesized nanostructures were

tested for solar light-driven photocatalytic conversion of the *p*-nitrophenol to *p*-aminophenol using water as a solvent and NaBH₄ as a reducing agent. The *p*-nitrophenol shows absorption maxima at 317 nm in water, which shifts to higher wavelength (400 nm) upon NaBH₄ addition due to the formation of phenolate ion of the light yellow color. The conversion progress was spectrophotometrically monitored; the intensity of the characteristic peak of *p*-nitrophenol at 400 nm depleted gradually with irradiation time accompanied by a parallel growth of a new peak at 298 nm (Fig. 4 & S1-S3) for *p*-aminophenol [31–32]. The absence of peaks at 388 or 302 nm due to 4-benzoquninoe monoxime or 4-nitrosophenol demonstrate the clean conversion process without generating any by product [33].

To study the effect of catalyst amount, an important parameter in catalysis, the amount of CdS nanosheets was varied from 5 mg to 20 mg keeping the other experimental conditions the same. A sharp rise in photoreduction rate of the *p*-nitrophenol was observed up to 15 mg, a dose at which approximately100% reaction occurred in 10 min (Fig. 5). However, beyond this amount (20 mg) the photoreduction rate was adversely affected (12 min). Low catalytic activity at high catalyst load can be explained in terms of particles aggregation (reduction in



Fig. 2. XRD pattern of CdS-1 (nanosheets) and CdS-2 nanorods.



Fig. 3. UV/Visible absorption spectra of CdS-1 and CdS-2 nanostructures.



Fig. 4. UV/Visible spectral changes associated with photoreduction of p-nitrophenol to p-aminophenol with irradiation time in the presence of (a) nanosheets and (b) nanorods.

the number of active catalyst sites), light scattering and screening effect of the dense particles, reducing the light flux received by the inner particles [34]. Furthermore, under similar conditions, 15 mg CdS nanorods were observed to do the conversion in 8 min (Fig. 4b), performance better catalytic than the nanosheets.

For both NPs, kinetics of the *p*-nitrophenol reduction was calculated using equations;

$$-dc/dt = k_{app} c \tag{1}$$

$$\ln\left(c/c_{o}\right) = -k_{app} t \tag{2}$$

where *t* is the reaction time and k_{app} is the apparent rate constant obtained from the plot of $\ln(c/c_o)$ vs *t* [35]. The linear correlation between $\ln(c/c_o)$ and *t* for both nanostructures (Fig. 6) suggest that the reduction of nitrophenol follows pseudo first order kinetics. The measured *k* values for nanosheets and nanorods are -0.3638 min^{-1} and -0.4035 min^{-1} , respectively confirming the relatively fast kinetics for the latter. It was further noted that k_{app} (-0.2028 min^{-1} to -0.3638 min^{-1}) increased by the gradual increase in the catalyst amount up to 15 mg, but diminished beyond this (-0.2727 min^{-1} at 20 mg).

The reusability or stability of a catalyst is a seminal factor for its practical application. In this work, the reusability of both catalysts was measured for 15 mg load (optimum amount) for three consecutive cycles.



Fig. 5. The photocatalytic conversion of *p*-nitrophenol to *p*-aminophenol with irradiation time at different catalyst (nanosheets) dose.

The results show slight decrease in photocatalytic activities in the initial cycle, though remain above 92% even in the 3rd cycle (Fig. 7). X-ray diffraction (XRD) patterns indicate that the crystal structure of both morphologies is undamaged after the reaction (Fig. S5). The better recyclability results and intact crystal structures before and after performing the activity designate stability of both NPs to photo-corrosion. Moreover, our results are comparable with the precious noble metals and better than the previously reported CdS (Table S1) [9,12–16,36]. The relatively high photocatalytic activity of both anisotrophically grown CdS morphologies can be most probably ascribed to higher quantum confinement effect that promotes the interfacial charge transfer, large surface area and good optical absorbance.

In summary, two cadmium (II) dithiocarbamates have been synthesized, characterized and then decomposed to CdS nanostructures via safe and simple one pot synthetic route. A balance between nucleation and growth, which in turns depends on the solubility and stability (thermolysis rate) of the precursors in en, has strongly affected morphology of the resultant nanostructures {2D nanosheets (CdS-1) and 1D nanorods (CdS-2)}. The X-ray diffraction pattern and HR-TEM image revealed that both morphologies have hexagonal crystal structure. The optical band gap of 2.91 eV (nanosheets) and 2.65 eV (nanorods), assessed from UV–Vis spectrum revealed their visible-light driven photocatalytic potential. The nanorods (CdS-2) were proved as a better catalyst than the nanosheets (CdS-1) for almost 100% conversion of the *p*-nitrophenol to *p*-aminophenol in water (8 min and 10 min, respectively). The photocatalytic behavior of CdS-1 and CdS-2



Fig. 6. The photoconversion kinetics of *p*-nitrophenol to *p*-aminophenol with irradiation time in the presence of CdS-1 (nanosheets) and CdS-2 (nanorods).



Fig. 7. Repetitive photocatalytic conversion of *p*-nitrophenol to *p*-aminophenol during three sequential cycles using 15 mg of catalyst dose of both CdS-1 and CdS-2 NPs.

is further merited by their recyclable nature (above 92% efficiency even after 3rd cycle) and stability (no change in XRD pattern after catalysis). In near future, we are planning to modify the CdS NPs surface with different co-catalysts for the purpose of promoting stability, charge generation and transportation; key parameters for tuning photocatalytic efficacy.

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Conflict of interest

The authors declare that they have no conflict of interest.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2017.03.033.

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